Anal. Calcd. for $C_{39}H_{30}O_3P_2Fe$: C, 70.6; H, 4.5; P, 9.3; Fe 8.4. Found: C, 70.6; H, 4.7; P, 9.2; Fe, 9.5.

The ethylcyclohexane solution was evaporated to dryness and the resultant residue dissolved in chloroform and chromatographed on alumina. Petroleum ether eluted a yellow oil having the same carbonyl frequencies in its infrared spectrum as $C_7H_8 \cdot Fe(CO)_2$. Chloroform eluted an unstable orange solution from which was obtained after crystallization and evaporation under nitrogen 0.4 g. (yield 13%) of a yellow-orange solid, $[(C_6H_5)_3P]_3Fe(CO)_2$. The latter exhibited intense carbonyl stretching modes at 1982 and 1923 cm.$^{-1}$ in carbon disulfide solution. As mentioned earlier, the relative intensities of the carbonyl bands depended on the extent of chromatography employed on $[(C_6H_5)_3P]_3Fe(CO)_2$ and on the method used to prepare the material.

Anal. Calcd. for $C_{56}H_{46}O_2P_3Fe$: C, 74.8; H, 5.1; P, 10.4. Found: C, 74.7; H, 5.9; P, 9.4.

10. **The Reaction between Triphenylphosphine and Butadiene–Iron Tricarbonyl or the Compound $C_8H_{10} \cdot Fe(CO)_3$.** (a) Butadiene–Iron Tricarbonyl.—Triphenylphosphine (1.3 g., 5.0 mmoles) was treated with butadiene–iron tricarbonyl[18] (5.0 mmoles) in the manner described above for similar reactions. A considerable amount of starting material was recovered, but in addition 60 mg. (4% yield based on $(C_5H_5)_3P$) of $[(C_6H_5)_3P]_8Fe(CO)_2$ (infrared spectrum identical with that observed previously for this compound) was obtained.

Anal. Calcd. for $C_{56}H_{45}O_2P_3Fe$: C, 74.8; H, 5.1; P. 10.4. Found: C, 74.3; H, 5.5; P, 9.1.

(b) **$C_8H_{10} \cdot Fe(CO)_3$.**—Treatment of triphenylphosphine (1.2 g., 4.7 mmoles) with $C_8H_{10} \cdot Fe(CO)_3$ (1.2 g., 4.7 mmoles) in the manner described above for similar reactions afforded starting materials and after several recrystallizations 150 mg. (11% yield) of $[(C_6H_5)_3P]_3Fe(CO)_2$ (infrared spectrum identical with that previously obtained for this compound except for relative band intensities).

Anal. Calcd. for $C_{56}H_{45}O_2P_3Fe$: C, 74.8; H, 5.1; P, 10.4 Found: C, 73.8; H, 5.6; P, 9.0.

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CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Organoboron Compounds. XII. Identification of the Presumed Alkoxydifluoroboranes as Coördination Compounds of Trialkyl Borates and Boron Fluoride[1,2]

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The substances reported in the literature as alkoxydifluoroboranes have properties which are more characteristic of coordination compounds than of substituted boranes. A consideration of vapor densities, cryoscopic molecular weights, distillation behavior, electric moments and reaction with nitrogen bases leads to the identification of the presumed alkoxydifluoroboranes as coördination compounds of trialkyl borates and two moles of boron fluoride. Comparison of these substances with the well established ether-boron fluoride coördination compounds supports their identification as coördination compounds.

A number of compounds formed by the reaction of boron fluoride with alcohols[3] or with alkyl borates[4-7] are identified in the literature as alkoxydifluoroboranes, $ROBF_2$.[8] These fluorine compounds are distillable without disproportionation while the alkoxydichloroboranes, $ROBCl_2$, undergo disproportionation and cleavage reactions when distilled.[9,10]

From a consideration of the relative disproportionation tendencies of other fluoro- and chloroboranes and analogous silicon compounds, it is not to be expected that alkoxydifluoroboranes would be more resistant to disproportionation than alkoxydichloroboranes. Where comparisons have been available it has been noted that disproportionation occurs much more readily with fluorine compounds than with chlorine compounds of boron and silicon. It has been found, for example, that dialkylchloroboranes are much more resistant to disproportionation (to alkyldichloroboranes and trialkylboranes) than are the dialkylfluoroboranes.[11] Also silyl chloride[12] is appreciably more resistant to disproportionation than is silyl fluoride and *sym* - tetraalkyldichlorodisiloxanes are much more resistant to disproportionation than are the corresponding fluorine compounds.[13] The case of the alkoxydihaloboranes would thus appear to represent a reversal of the comparative tendencies toward disproportionation noted in other boron and silicon compounds. Since we are currently engaged in a general study of the disproportionation reactions of organoboron and organosilicon compounds in this Laboratory, the presumed alkoxydifluoroboranes were examined to check their apparent anomalous resistance to disproportionation. The results obtained indicate that the presumed alkoxydifluoroboranes have been incorrectly identified and that the resistance to disproportionation of these substances does not, therefore, represent a reversal of the general trend.

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(2) Contribution from the Radiation Project operated by the University of Notre Dame and supported in part under Atomic Energy Commission Contract AT-(11-1)-38.

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Experimental

Preparation and Purification of Trialkyl Borates.—All liquid reagents and products were fractionally distilled through a 60-cm., glass-helix packed column.

Trimethyl borate was treated with lithium chloride,[14] decanted and distilled. The fraction distilling at 68.0–68.2° was used. Triethyl and tri-*n*-butyl borate were prepared by standard procedures from boric oxide and the corresponding alcohols and were purified by fractional distillation. Only sharp boiling fractions were used.

Reaction of Boron Fluoride with Trialkyl Borates.—Triethyl borate (40 g., 0.274 mole) was transferred to a dry 100-ml., round-bottom flask by means of dry nitrogen pressure. Boron fluoride, bubbled through concentrated sulfuric acid saturated with boric oxide,[15] was absorbed completely when passed into the triethyl borate. The absorption of boron fluoride was exothermic and the reaction mixture was cooled in an ice-bath. The boron fluoride was passed in at such a rate that, in a period of 1.5 hours, 37.5 g. (0.552 mole) of gas was absorbed. The reaction mixture, which was protected by a drying tube from pick-up of atmospheric moisture, remained colorless or in some instances turned slightly yellow on absorption of boron fluoride and increased noticeably in volume. When exactly two moles of boron fluoride had been absorbed per mole of triethyl borate, unreacted gas began to pass through the reaction mixture and addition of gas was stopped. The weighed reaction mixture was distilled at constant temperature with essentially quantitative recovery of product. The physical properties observed for an early fraction are listed in Table I. During distillation a slight evolution of boron fluoride was observed. Although the boiling point was constant, successive fractions showed a small gradual increase in index of refraction and decrease in density and fluorine content.

TABLE I

PROPERTIES OF COMPOUNDS

Compound	$(MeO)_3B{\cdot}2BF_3$	$(EtO)_3B{\cdot}2BF_3$	$(n\text{-}BuO)_3B{\cdot}2BF_3$
M.p., °C.	37.0–39.5	19–21	....
B.p., °C. (mm.)	85.2–85.4 (745)	82.4–82.7 (745)	51.5–51.8 (26)
n^{25}D	....	1.3495	1.3835
d^{25}	....	1.2452	1.1302
Fluorine, %			
Calcd.	47.6	40.4	31.1
Obsd.	46.5	37.9	29.9
Boron, %			
Calcd.	13.5	11.7	8.9
Obsd.	12.7	11.6	9.3
Mol. wt.			
Calcd.	239.4	281.6	366.7
Obsd.	242	282	356

Using the same procedure 20 g. (0.192 mole) of trimethyl borate was reacted with boron fluoride. Twenty-six g. (0.38 mole) of boron fluoride was absorbed. Near the end of the reaction a white solid formed and the mixture slowly solidified. The product was purified by distillation. The observed physical constants are listed in Table I.

n-Butyl borate (45 g., 0.195 mole) was reacted as above with boron fluoride and 25 g. (0.370 mole) of boron fluoride was absorbed. Product (33 g.) was collected at 51.5–51.8° at 26 mm. Physical properties are listed in Table I. A small middle fraction was collected and 26 grams of *n*-butyl borate was collected at 97.4–99.8° (7.8 mm.). During the distillation there was apparently a considerable loss of boron fluoride as indicated by the relatively low yield of reaction product and the recovery of *n*-butyl borate.

Physical Properties and Analyses.—Refractive indexes were obtained at 25° with an Abbe refractometer which had been flushed with dry nitrogen. Densities were obtained at 25° using a 2- or 5-ml. Lipkin pycnometer flushed with dry nitrogen and filled under nitrogen pressure. Vapor densities were obtained by the Dumas method. Boron and fluorine analyses were done by the method of Booth and Martin.[16]

Molecular Weights.—Cryoscopic molecular weight determinations in benzene, cyclohexane and dioxane were carried out as described previously.[17] The benzene was dried over phosphorus pentoxide and distilled. The molal freezing point depression for benzene, 5.02, was obtained by using sublimed naphthalene. The K_f value for cyclohexane was similarly found to be 20.2. Previously purified dioxane was freshly distilled over sodium and the K_f value, 4.9, was used for dioxane solutions.

Eight determinations in benzene were carried out for the triethyl borate–boron fluoride reaction product over a concentration range of 18.02 to 46.72 g. solute per 1000 g. solvent. The molecular weight values obtained range from 260 to 302 to give an average value of 282. The lowest and highest values observed differed from the average by less than 8%. The average of two determinations in cyclohexane was 316. The calculated value for $(EtO)_3B{\cdot}2BF_3$ is 281. Two determinations in dioxane at concentrations of 26.16 and 28.77 g. solute per 1000 g. solvent gave an average value of 109 for the molecular weight. The value calculated on the assumption that the complex dissociates completely in dioxane is 94.

Determination of the molecular weight of the methyl borate–boron fluoride reaction product in benzene using a concentration range of 17.95 to 36.7 g. solute per 1000 g. solvent gave molecular weight values from 227 to 258 with an average value of 242; calcd. for $(MeO)_3B{\cdot}2BF_3$: 239. Four determinations in benzene for the *n*-butyl borate product with a concentration range of 27.92 to 57.6 g. solute per 1000 g. solvent gave molecular weight values from 350 to 361 with an average value of 356; calcd. for $(BuO)_3B{\cdot}2BF_3$: 366.

Dipole Moments.—The electric moment of the ethyl compound was obtained as reported previously.[18] The cell was calibrated with dry benzene, $\epsilon = 2.273$. The average density of the benzene was 0.8742 at 25°. Solutions for measurement were prepared in baked glassware and transferred under dry nitrogen pressure. The weight fraction range was from 0.00391 to 0.01054. The molar polarization for the compound at infinite dilution was calculated from the Hedestrand equation as modified by LeFevre and Vine[19] using an extrapolated value for $\Delta\epsilon/wf_2$. Table II lists the weight fractions, dielectric constants, densities and dielectric and density ratios of the solutions used. Dipole moments in Debye units were calculated from the Debye equation

$$\mu = 0.221\sqrt{P_{2\infty} - 1.05MR\text{D}}$$

at 25°, taking the atomic polarization as 5% of the molar refraction. The molar refraction for the compound was calculated from the observed index of refraction and density as given in Table I. The value thus obtained was 48.65 ml. This calculation gave a dipole moment of 4.7 ± 0.1 *D* for the triethyl borate–boron fluoride reaction product.

TABLE II

WEIGHT FRACTIONS, DIELECTRIC CONSTANTS, DENSITIES AND DIELECTRIC AND DENSITY RATIOS OF BENZENE SOLUTIONS

wf_2	ϵ	d^{25}	$\Delta\epsilon/wf_2$	$\Delta d/wf_2$
0.00391	2.2854	0.8748	5.88	0.1535
.00396	2.2896	....	6.89	....
.00663	2.3011	.8755	5.87	.1962
.00669	2.3026	....	4.43	....
.00961	2.3142	....	4.29	....
.01054	2.2946	.8764	3.07	.2087

Reaction of Nitrogen Bases with the Triethyl Borate–Boron Fluoride Reaction Product.—Distilled triethyl borate–boron fluoride reaction product (12 g., 0.043 mole) was transferred by means of dry nitrogen pressure to a 100-ml. round-bottom flask and was diluted with 25 ml. of dry benzene. Ammonia previously treated with metallic sodium was bubbled at a moderately rapid rate through a sodium hydroxide tube into the benzene solution cooled in ice-

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water. The white precipitate formed was separated from liquid by decantation and dried under vacuum (m.p. 175–180°; lit. for $NH_3 \cdot BF_3$,[20] 180°). The decanted liquid was distilled through a 30-cm. nichrome-packed column and gave essentially quantitative recovery of triethyl borate (b.p. 118°; $n^{25}D$ 1.3735; d^{25} 0.8571). Addition of excess ammonia caused the precipitate to become gummy or to dissolve. Attempts to use ether as the solvent in the reaction were unsatisfactory since the product is soluble in ether to a considerable extent.

Distilled triethyl borate–boron fluoride reaction product (14 g., 0.050 mole) in 20 cc. of dry benzene was transferred dropwise by means of dry nitrogen pressure into 7.8 g. (0.099 mole) of pyridine in 20 cc. of benzene cooled in ice-water. A white precipitate formed which was separated as above and dried under vacuum over concentrated sulfuric acid (m.p. 45–50°; lit. for $py \cdot BF_3$,[21] 47–48°).

In other instances the above reactions were done in the absence of solvent with essentially the same results.

Discussion

Gasselin,[3] who first prepared the compounds presumed to be alkoxydifluoroboranes, characterized them on the basis of elemental analysis and vapor phase molecular weights only. The composition and vapor density observed by Gasselin were reasonably interpreted to indicate that the substances were alkoxydifluoroboranes and that they were monomeric at least in the vapor state. Apparently because of the statement made by Gasselin that the compounds were insoluble in hydrocarbons, no cryoscopic molecular weight determinations on the methyl or ethyl compounds have been reported previously.

We have found that the compounds formed by the reaction of boron fluoride with trimethyl and triethyl borate are readily soluble in benzene and in cyclohexane. Our cryoscopic data on the presumed alkoxydifluoroboranes show without question that the molecular weights in benzene and in cyclohexane are three times the values for monomeric alkoxydifluoroboranes. These cryoscopic determinations were carried out repeatedly over an appreciable concentration range, and the freezing point constants used and the procedure were checked with pure compounds of known molecular weight. The freezing point apparatus was protected against pick-up of atmospheric moisture.

The molecular weights obtained for these compounds require that they be formulated either as trimeric alkoxydifluoroboranes, or as coördination complexes of composition $(RO)_3B \cdot 2BF_3$, both of which have the same molecular weight. The vapor density molecular weight found by Gasselin and checked by the authors is reconcilable with either formulation if it is assumed that the coördination complexes are completely dissociated in the vapor state. Nearly complete dissociation of the triethyl borate–boron fluoride complex also occurs in solution in dioxane. Cryoscopic molecular weight determinations for the ethyl compound in dioxane gave an observed molecular weight of 109. The molecular weight, calculated on the assumption that complete dissociation into triethyl borate and dioxane–boron fluoride occurs, is 94.

Allen and Sudgen[5] concluded from parachor determinations that the methyl compound was dimeric in the liquid state. Goubeau and Lucke[6] came to the same conclusion on the basis of the Trouton constant which they found to be about twice the normal value. In connection with the conclusion of Goubeau and Lucke that the Trouton constant indicated a dimeric liquid, the results of Laubengayer and Finlay[22] on ether–boron fluoride complexes are significant. These workers found that the Trouton constants for methyl ether–boron fluoride and ethyl ether–boron fluoride were 30.5 and 32.8, respectively, approximately 1.5 times the values for normal liquids.

In the case of the ether–boron fluoride complexes it has been shown by Brown and Adams[23] that extensive dissociation takes place on vaporization. Thus the enthalpy change observed in the case of the ether–boron fluoride complex includes heat of dissociation as well as heat of vaporization and is not therefore a valid measure of the molecular complexity in the liquid state. If then, as our results indicate, the presumed alkoxydifluoroboranes are actually coördination complexes of trialkyl borates with boron fluoride, the conclusion as to molecular complexity based on a Trouton constant value is of questionable validity. It is interesting to observe that an apparent higher Trouton constant for the trialkyl borate–boron fluoride complex than for the ether complex is reasonable, since the heat of dissociation of a molecule with two donor–acceptor bonds would be expected to be greater than that of a molecule with one such bond if the individual bond strengths are not greatly different.

A comparison of the relative boiling points of methyl ether–boron fluoride (b.p. 126.9°) and ethyl ether–boron fluoride (b.p. 125.7°) shows that these compounds boil very close to each other and that the methyl compound has a slightly higher boiling point than the ethyl compound. A similar closeness of boiling points is observed for the substances which we now formulate as $(MeO)_3B \cdot 2BF_3$ (b.p. 85.4°) and $(EtO)_3B \cdot 2BF_3$ (b.p. 82.7°) and again the methyl compound has a slightly higher boiling point than the ethyl compound. Thus the distillation behavior of the presumed alkoxydifluoroboranes, by analogy to the known ether–boron fluoride complexes, favors their formulation as coördination complexes of trialkylborates with boron fluoride.

The observed and calculated molar refractions for the products of the reaction of trimethyl borate and triethyl borate with boron fluoride also are consistent with their formulation as coördination complexes. Using 1.67[13] for the boron–oxygen bond refraction in trialkylborates, 6.00 for boron fluoride[24] and Denbigh's[25] values for the remaining bonds gives for the ethyl compound MR_D calcd. 50.64, MR_D obsd. 48.65. The observed molar refraction is thus much lower than the value calculated without consideration of the influence of a possible coördinate bond. A similar lowering of observed molar refraction has been noted for the ethyl ether–boron fluoride coördination compound.[22]

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Further evidence that the compounds are boron fluoride coördination complexes, which dissociate extensively on vaporization, is provided by the observation that slow fractional distillation of the triethyl borate–boron fluoride complex in a packed column results in a small but detectable loss of boron fluoride. While distillation temperatures show no appreciable variation, the fluorine analyses are generally significantly lower than the theoretical after several distillations. While the theoretical fluorine percentage for $(EtO)_3B \cdot 2BF_3$ is 40.4 the fluorine percentages after distillation were observed to range from 37.9 to 37.0. Refluxing of the ethyl compound for a half-hour period before distillation gave early fractions boiling at the same temperature as later fractions, but having appreciably lower fluorine percentages. The fractional distillation of a liquid of composition $(n\text{-BuO})_3B \cdot 2BF_3$, resulted in a first fraction with a fluorine content of 29.9% (calcd. for $(n\text{-BuO})_3B \cdot 2BF_3$, 31.1%). Subsequent fractions showed decreasing fluorine content and a final fraction of essentially pure *n*-butyl borate was obtained.

The electric moment obtained for the triethyl borate–boron fluoride product in benzene points quite conclusively to the identification of the compound as a coördination complex rather than an alkoxydifluoroborane.[26] The value obtained for the ethyl compound, 4.7 ± 0.1 *D*, may be compared with the values 4.97[18] and 5.29[27] reported for ethyl ether–boron fluoride and with the values found for *n*-amyldifluoroborane[16] in benzene, 1.64 *D*, and in dioxane, 3.37 *D*.

The electric moment of a coördination complex of trialkyl borate with boron fluoride would be expected to be close to that for ether–boron fluoride and for an alkyldifluoroborane in the donor solvent dioxane. The electric moment for a monomeric alkoxydifluoroborane in benzene would be expected to be considerably less than that of an alkyldifluoroborane. A trimeric cyclic alkoxydifluoroborane should have an even smaller moment.

The reactions of the presumed alkoxydifluoroboranes with ammonia and pyridine result in the immediate formation, even at ice-bath temperatures, of the boron fluoride adduct and the quantitative liberation of trialkyl borate. This result was observed in this Laboratory and has also been reported previously in the literature.[4,7] The formation of a boron fluoride adduct from the reaction of a presumed alkoxydifluoroborane with nitrogen bases was explained by Lappert[7] as resulting from the rapid and complete disproportionation of the alkoxydifluoroborane apparently induced by the action of the nitrogen base. A consideration of the probable mechanism of the disproportionation reaction makes the above explanation unsatisfactory. Any reasonable mechanism for a disproportionation reaction which occurs rapidly at low temperatures must allow for a low activation energy. A monomolecular reaction would involve the breaking of strong chemical bonds at low temperatures and therefore seems improbable. A bimolecular mechanism which involves the interaction of an oxygen atom of one molecule with the vacant p orbital of the boron on a second molecule appears much more probable for the disproportionation reaction. Such a reaction path, involving the availability of a vacant p orbital on a boron atom, would be blocked by the action of a nitrogen base and would result in the formation of $ROBF_2 \cdot R_3N$ and no liberation of trialkyl borate.

While the reaction of boron fluoride with trialkyl borates (boric acid esters) results in the formation of a coördination complex which is stable at ordinary temperatures and is dissociated into its components at higher temperatures, the reaction of boron fluoride with esters of alkylboronic acids, $RB(OR)_2$, is reported by Brindley, Gerrard and Lappert[28] to take a different course. These workers found that the coördination complex of di-*n*-butyl-*n*-butylboronate and boron fluoride, which may be assumed to be formed as the initial step in the reaction of the boronate and boron fluoride, rapidly decomposes at ordinary temperatures to give *n*-butyldifluoroborane and the compound identified in the present work as $(BuO)_3B \cdot 2BF_3$.

The difference in the behavior of the boron fluoride coördination complexes of boric acid esters and boronic acid esters is probably due to the difference in the stabilities of the decomposition products. *n*-Butyldifluoroborane which results from the decomposition of the boronic acid ester–boron fluoride complex is a very stable compound which has been shown[29] to be completely resistant to disproportionation. The corresponding decomposition product of the boric acid ester–boron fluoride complex would be an alkoxydifluoroborane which, as has been shown herein, is unstable with respect to the trialkyl borate–boron fluoride coordination complex from which it would be formed.

NOTRE DAME, INDIANA

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